

REACTIONS OF URANIUM AND THE PLATINIDE ELEMENTS

II. The Uranium-Rhodium System

by

John J. Park

ABSTRACT

The phase diagram of the uranium-rhodium system was constructed from data obtained by thermal analysis, metallographic examination, and X-ray diffraction. The system is characterized by four intermetallic compounds: U_4Rh_3 , formed peritectically at 1155°C and having a solid state transformation at 720°C; U_3Rh_4 , formed peritectically at 1450°C; U_3Rh_5 , formed peritectically at 1550°C; and URh_3 , melting congruently at 1700°C. One eutectic occurs at 865°C and 24.5 a/o rhodium, and a second at 1393°C and about 87 a/o rhodium. The maximum solid solubility of rhodium in uranium is 8 a/o, and of uranium in rhodium is 3 a/o.

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II. THE URANIUM-RHODIUM SYSTEM*

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1. INTRODUCTION

This report is one of a group concerned with the binary equilibrium diagrams of uranium with the individual elements of the platinide group, Group VIII of the periodic chart, conducted for the Atomic Energy Commission. The results of these studies has resulted in a correlation between atomic radius, solid solubility, and the crystal lattice of the solvent to be presented in the final report of this series. The data were obtained by thermal analysis, metallographic examination, and X-ray diffraction, which were combined to produce this proposed phase diagram.

2. PREVIOUS WORK

Some information on the uranium-rhodium system had appeared in the compilation of the constitution diagram of uranium and thorium alloys by Rough and Bauer ^{(1)†}, including information obtained for this paper. No information on this system was included in the compilation by Hansen and Anderko ⁽²⁾, but information on various portions of the system has appeared in reports from the Argonne National Laboratory Metallurgy Division ^(3, 4, 5).

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†Figures in parentheses indicate the literature reference at the end of this paper.

3. PREPARATION OF ALLOYS

The alloys used in the study of this system were prepared by arc melting or by induction melting in beryllia crucibles. In general, the alloys of low rhodium content were made by induction melting, though arc melting was utilized in diluting certain alloys of low rhodium content. No evidence of gross contamination by beryllia was noted in the as-cast alloys or in those which had been later heated on a beryllia crucible for melting point determinations.

The rhodium was obtained from J. Bishop & Co. as powder which was compressed into pellets for later melting. The powder was about 99.9 percent purity, and the spectrochemical analysis of the material indicated the following major impurities and the estimated amounts: 0.01-0.1% Fe, Ir, Pd, Pt; 0.001-0.01%, Cu, Mg, Ni, Ru, Si, Sn; and 0.0001-0.001% Ag, Al, Ca.

The thermal analyses, metallographic preparation, and X-ray diffraction procedures were identical to those employed in the study of the uranium-ruthenium system⁽⁶⁾. Analysis of the alloys was carried out as described by Maienthal⁽⁷⁾.

4. EXPERIMENTAL RESULTS

4.1 The Uranium Solid Solution Regions

The solid solubility of rhodium in the respective uranium lattices was determined principally by metallographic examination of quenched specimens but some data were obtained dilatometrically⁽⁸⁾. The specimens utilized for quenching had been homogenized for about 200 hours at 825°C; the alloys were then sectioned and small specimens were sealed in silica tubing under a partial pressure of helium.

Thermal analysis data of alloys of low rhodium content revealed that the addition of rhodium to uranium lowers the melting point of uranium and also depresses the uranium transformations. The thermal analysis data are listed in Table I for alloys of up to 10.8 atomic percent (a/o) rhodium.

The data show the decrease in melting point of the alloys, and they also indicate that the gamma-beta transformation is lowered to about 683°C and the beta-alpha transformation to about 625°C. These results are almost identical with the data for the uranium-ruthenium system presented previously. The apparent solid solubility of rhodium in alpha-uranium is less than 0.5 a/o and the solid solubility of rhodium in beta-uranium is higher and on the order of 1 to 2 a/o as indicated by thermal analysis, though quenched specimens were used in determining the phase fields more closely.

Data on the uranium transformations had been obtained from dilatometric measurements⁽⁸⁾. The data from the dilatometric measurements confirm the the results from thermal analysis, for those data indicated that the alpha-beta transformation had apparently stabilized on cooling at 625°C. Extrapolation to the intersection of the line connecting the uranium and the 0.36 a/o rhodium alloy transformation temperature with the line at 625°C suggests that the rhodium solubility in the alpha lattice is on the order of 0.2 a/o.

Quenched specimens were utilized for a more exact determination of the solid solution fields. In many of the quenched specimens, particularly near the expected beta plus gamma region, the appearances and the X-ray data confirmed the tentative conclusions from the thermal analysis data. The extent of the solid solubility of rhodium in alpha-uranium is quite limited, as indicated by the

appearance of a considerable amount of precipitate phase in the thermal analysis sample of 0.6 a/o rhodium. Quenched specimens of lesser rhodium content, due to small amounts of impurity precipitate, could not unambiguously be determined as single phase specimens. However, the accumulated data indicate that the maximum solid solubility of rhodium in alpha-uranium is definitely less than 0.5 a/o, and it is probably on the order of 0.2-0.3 a/o.

Additional quenched specimens aided in determining the boundaries between the higher temperature phase fields. The sample of 0.77 a/o rhodium, using a number of quenched specimens, each of which gave only the alpha-uranium X-ray diffraction peaks, exhibited two phases (alpha plus compound) at 625°C, a single phase (originally beta) at 675° and 720°C, two phases (beta plus gamma) at 737°C, and a single phase from 760° to near 1105°C, in which melting appeared. In this particular alloy, beta-uranium could not be retained by quenching to room temperature; the conclusions of the presence of beta- or of gamma-uranium were based on the appearance and distribution of the phases in the etched specimens. The data from metallographic observations and thermal analysis place the maximum solid solubility of rhodium in beta-uranium at about 1.5 a/o and in gamma-uranium at very close to 8 a/o.

Certain of the X-ray patterns indicated the presence of beta-uranium in the quenched specimens. In fact, the retention of beta-uranium was most easily accomplished by quenching from near the solidus, for the alloys of 1.7, 2.3, and 4.0 a/o rhodium quenched from the 1070-950°C range each had retained beta-uranium. In two other specimens, the 1.1 a/o rhodium alloy at 737°C and the 1.8 a/o rhodium at 747°C, beta-uranium was present. In no instance was the gamma-uranium pattern detected.

The gamma-uranium eutectoid composition is apparently very close to 5.6 a/o rhodium, for specimens of this composition quenched from 600° and 670°C were almost completely decomposition products though the 710°C sample was not. The 670°C sample contained alpha-uranium, but the diffraction pattern was not sharp.

4.2 The Region of 0-50 a/o Rhodium

The addition of rhodium to uranium results in a lowering of the freezing point of uranium and a depression in the uranium transformation temperatures. As mentioned above, the gamma-beta uranium transformation is lowered to 683°C and the beta-alpha transformation to 625°C. The eutectic composition, as determined from the trend of the freezing points is near 24.5 a/o rhodium and the eutectic temperature is 865°C. The thermal analysis data for this series of alloys are presented in Table II and in Figure 1.

The thermal analysis data indicate that the eutectic arrest is detected in alloys of from 20.5 to 40.7 a/o rhodium. Confirmation of the eutectic was obtained from metallographic examination of two sets of specimens ranging from 24.4 to 40.7 a/o rhodium which had been held at 870° and at 853°C for 25 hours. In each of the four alloys, a considerable difference existed between the appearance of the alloys at 853° and at 870°C (Fig. 2a,b), for at the higher temperature fusion was evident. The alloy of 43.4 a/o rhodium was held at 935°C for 90 hours with no evidence of fusion. In fact, this specimen was almost a single phase following the thermal analysis run (Fig. 2c), which further indicates the existence of a compound near this composition. The detection of the uranium transformations during the heating and cooling traces of the thermal analysis charts in alloys

of up to 40.7 a/o rhodium further establishes that the first compound adjacent to the uranium solid solution fields is between 40.7 and 43.4 a/o rhodium. This compound has been placed at the U_4Rh_3 composition (42.8 a/o rhodium). The presence of the arrest near 720°C is apparently a solid-state transition within this phase; however, the heat treated and quenched specimens gave only one X-ray pattern, that for the room temperature structure, whose d-spacings are listed in Table III. The presence of the thermal analysis arrests near 1155°C in the 43.4 and the 50.8 a/o rhodium alloys are from the peritectic reaction of the U_4Rh_3 phase. No evidence of eutectic areas was seen in specimens in this composition range, nor in alloys of up to near 57 a/o rhodium.

4.3 The Region of 50-75 a/o Rhodium

The alloys between 50 and 57 a/o rhodium presistently gave similar X-ray diffraction patterns, and one particular pattern was most strong in alloys near the 57 a/o rhodium composition. The alloy of 50.8 a/o rhodium was definitely two phase in all heat treated specimens but the alloy of 57.4 a/o rhodium was almost a single phase. The combination of X-ray diffraction data and the metallographic appearance of the specimens placed the compound at the U_3Rh_4 composition. The reaction observed near 1450°C by thermal analysis and melting point determinations is apparently the peritectic reaction for this particular compound. The X-ray diffraction pattern has been determined and is also listed in Table III.

An additional compound at 62.5 a/o rhodium, U_3Rh_5 , is formed in this region. This particular phase was detected by X-ray diffraction in alloys between 62.5 and 74.5 a/o rhodium, and the diffraction pattern is given in Table III. The alloy of 62.5 a/o rhodium was heated by induction and it appeared to react near 1550°C

and to be wholly molten at about 1600°C. Other alloys of higher rhodium content had melting points which tended toward a maximum near 1700°C at the 75 a/o rhodium composition. The melting point determinations for alloys of from 60.7 to 74.9 a/o rhodium are listed in Table IV, and these data indicate that the U_3Rh_5 compound forms peritectically at about 1550°C.

X-ray patterns from powder filed from the as-cast (arc melted) alloys of 60.7 and 74.9 a/o rhodium contained lattice spacings which were indexed as a cubic phase with lattice dimensions of approximately 4.00 Å. These data compare very well with the values for the URh_3 phase, $a = 3.991$ Å, as reported by Dwight, Downey, and Conner ⁽⁹⁾. However, upon heat treatment and the attaining of chemical equilibrium of the 60.7 a/o rhodium alloy, this phase gradually disappeared, and it was retained only in homogenized alloys of greater than 62.5 a/o rhodium.

5. THE REGION OF 75-100 A/O RHODIUM

The melting point determinations of alloys of compositions between 75 and 100 a/o rhodium showed an obvious depression to an apparent eutectic composition. Alloys of less than 75 a/o rhodium were tending toward a maximum, and the melting point of the 74.9 a/o rhodium alloy was at 1690°C, while the alloy of 79.7 a/o rhodium had a melting point of 1570°C. These data indicate that the URh_3 compound melts congruently at approximately 1700°C. The data from thermal analysis and from the melting point determinations are listed in Table V.

The eutectic composition, as determined from the melting point information of the alloys is located near 87 a/o rhodium, and the eutectic temperature is

near 1400°C. The thermal analysis chart of the 89.3 a/o rhodium sample showed a strong arrest at 1393°C, which fits very well with the other data, and this temperature has been taken as the eutectic temperature.

The solid solubility of uranium in rhodium is between 2.3 and 4.6 a/o uranium, for the alloy of 97.7 a/o rhodium which had been heated for 20 minutes at 1600°C was single phase while the alloy of 95.4 a/o rhodium was not. The diffraction patterns of these alloys showed broad peaks which prevented an accurate determination of the lattice spacings. The maximum solid solubility of uranium in rhodium is believed to be on the order of 3 a/o. The complete diagram for this system is presented in Figure 3.

6. SUMMARY OF THE URANIUM-RHODIUM SYSTEM

The addition of rhodium to uranium results in the depression of the liquidus to a eutectic at 24.5 a/o rhodium and 865°C and also lowers the gamma-beta uranium transformation to 683°C and the beta-alpha transformation to 625°C. The U_4Rh_3 compound is formed peritectically from liquid and U_3Rh_4 at 1155°C, and it has a solid-state transformation at 720°C. The U_3Rh_4 compound is formed peritectically from liquid and U_3Rh_5 at 1450°C, and U_3Rh_5 is formed peritectically from liquid and URh_3 . The URh_3 compound melts congruently at 1700°C. URh_3 and rhodium react to form the eutectic mixture at 87 a/o rhodium and 1393°C.

The maximum solid solubility of rhodium in gamma-uranium is near 8 a/o, in beta-uranium is about 1.5 a/o, and in alpha-uranium is about 0.2 a/o. The solid solubility of uranium in rhodium is about 3 a/o.

REFERENCES

1. F. A. Rough and A. A. Bauer, U. S. AEC Publication BMI-1300, also Constitutional Diagrams of Uranium and Thorium Alloys, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1959).
2. M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill Book Co., Inc. (1958).
3. A. E. Dwight, Argonne National Laboratory ANL-5797, p. 51 (1957).
4. A. E. Dwight, Argonne National Laboratory ANL-5837, p. 54 (1957).
5. M. V. Nevitt, A. E. Dwight, and S. T. Zegler, Argonne National Laboratory ANL-5975, p. 53 (1958).
6. John J. Park, Submitted for publication in J. Res. NBS.
7. E. June Maienthal, Anal. Chem. 35, 1094 (1963).
8. J. J. Park, and B. T. Sanderson, NBS Report 8025 (1963).
9. A. E. Dwight, J. W. Downey, and R. A. Conner, Jr., Acta Cryst. 14, 75 (1961).

TABLE I
THERMAL ANALYSIS RESULTS, U-Rh
Alloys of 0-10.8 a/o Rhodium

Arrests °C				
a/o Rh	Fusion	Arrest	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$
0	1131		767	657
0.6	1107		746	630
1.7	1115		735	635
3.3	(above 960)		690	628
5.6	1049		673	624
10.8	1008	723	682	630

TABLE II
THERMAL ANALYSIS RESULTS, U-Rh
Alloys of 0-50.8 a/o Rhodium

Arrests °C							
a/o Rh	Arrest	Arrest	Fusion	Eutectic	Arrest	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$
0			1131			767	657
0.6			1107			746	630
1.7			1115			735	635
3.3			(above 960)			690	628
5.6			1049			673	624
10.8			1008		723	682	630
20.5			897	872	721	690	629
24.2				870	725	680	625
33.4			1000	865	725	685	626
36.6			1072	856	721	680	616
40.7				861	708	684	610
43.4		1156			719		
50.8	1440	1154					

TABLE III
X-RAY DIFFRACTION DATA, INTERPLANAR SPACINGS, U-Rh

U_4Rh_3		U_3Rh_4		U_3Rh_5	
d	I	d	I	d	I
3.17	vw	3.16	vw	2.62	m
2.66	m	2.46	w	2.44	w
2.60	vs	2.40	s	2.36	m
2.55	w	2.25	w	2.22	s
2.50	m	1.86	m	2.14	w
2.27	vw	1.73	s	2.12	w
2.22	w	1.51	w	2.04	m
2.16	w	1.39	m	1.92	m
2.06	vw	1.28	w	1.67	vw
1.82	w	1.26	m	1.49	w
1.80	s	1.14	m	1.44	vw
1.66	m	0.99	m	1.35	w
1.58	vw			1.31	m
1.56	vw			1.17	vw
1.53	w			1.14	vw
1.48	w			1.02	m
1.42	vw				
1.40	vw				
1.38	vw				
1.30	vw				
1.24	vw				
1.14	w				

TABLE IV
MELTING POINT DETERMINATIONS
Alloys of 60.7-74.9 a/o Rhodium

a/o Rh	Optical Pyrometer Reading, °C
60.7	1450
62.5	1550 (reaction)
62.5	1600 (molten)
69.8	1675
74.9	1690

TABLE V
THERMAL DATA, RHODIUM-RICH ALLOYS
Alloys of 75-100 a/o Rhodium

A. Thermal Analysis	
a/o Rh	Thermal Arrests, °C
84.0	1467
89.3	1393
B. Melting Point Determinations	
a/o Rh	Melting Point, °C
74.9	1690
79.7	1570
88.2	1500
89.3	1505
95.4	1750
97.8	1850

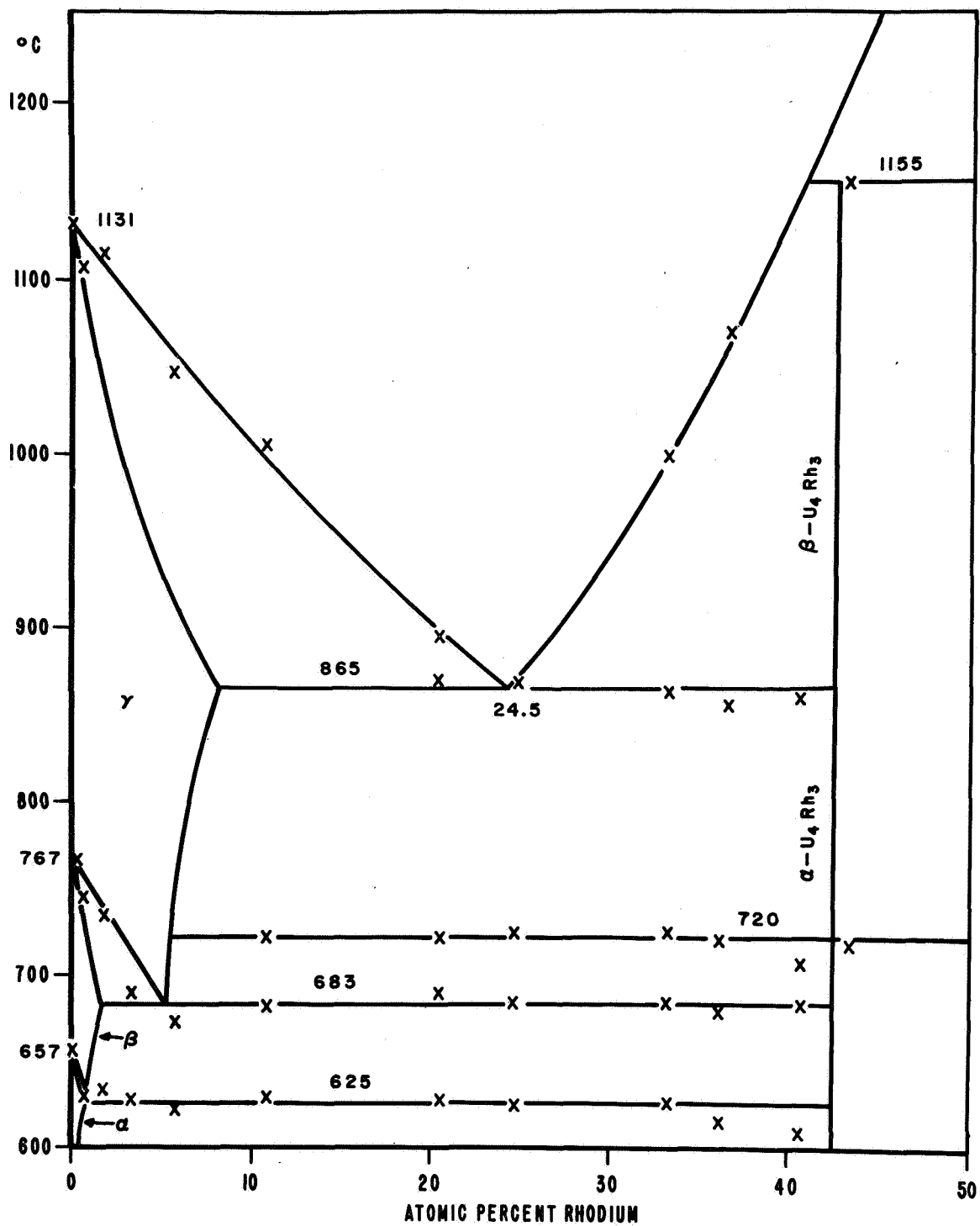
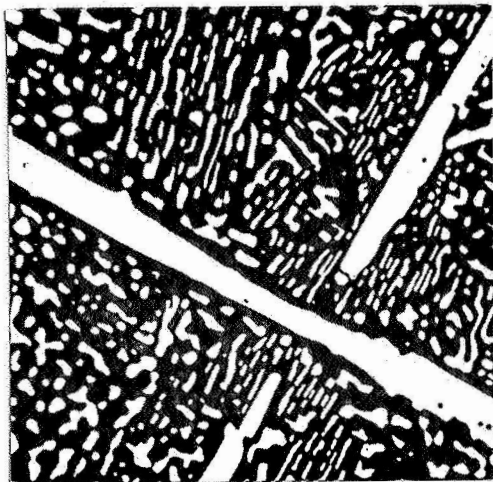
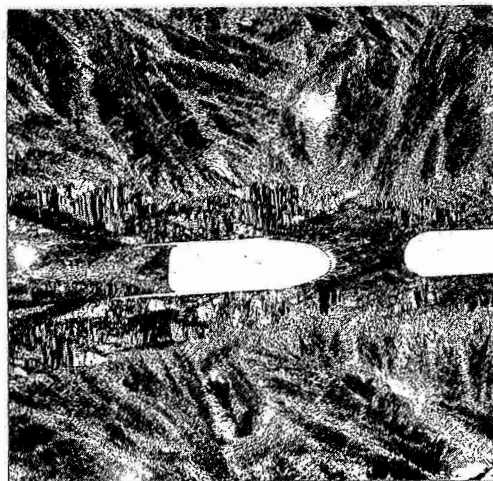


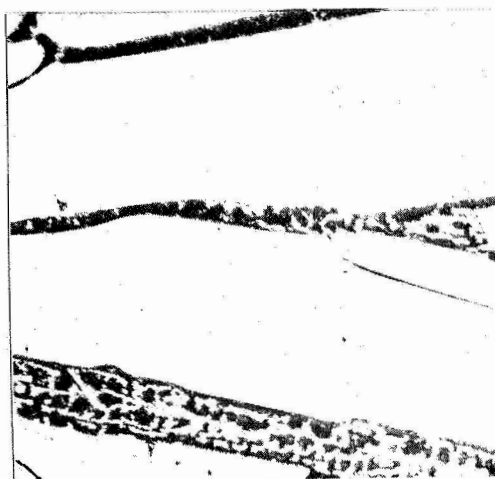
Figure 1—Uranium-Rich Portion of U-Rh System



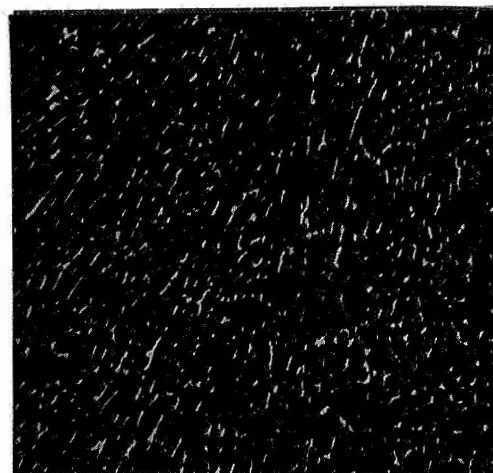
(a)



(b)



(c)



(d)

Uranium-rhodium alloys

- (a) Alloy of 24.2 a/o rhodium held at 853°C for 25 hours.
Glycol etch. X 100
- (b) Alloy of 24.2 a/o rhodium held at 870°C for 25 hours.
Glycol etch. X 100
- (c) Alloy of 43.4 a/o rhodium held at 935°C for 90 hours.
Glycol etch. X 50
- (d) Alloy of 57.4 a/o rhodium held at 935°C for 90 hours.
Nitric acid etch. X 100

Figure 2—Uranium Rhodium System

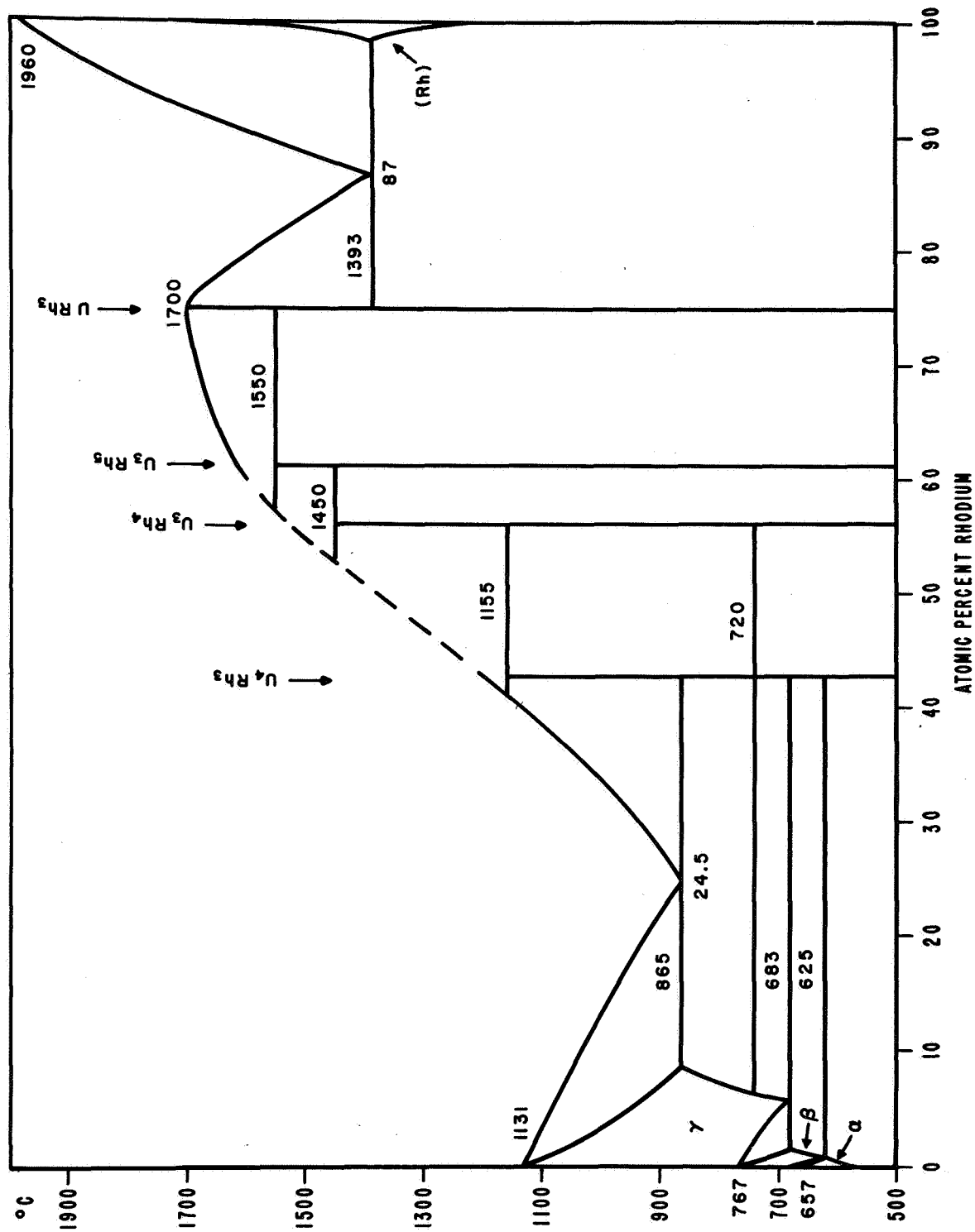


Figure 3-Uranium-Rhodium System